Journal of Organometallic Chemistry, 65 (1974) C43—C45

Preliminary communication

SOME ADDUCTS OF $RhCl[P(C_6H_{11})_3]_2$, A RHODIUM COMPOUND SPONTANEOUSLY COORDINATING DINITROGEN

H.L.M. VAN GAAL, F.G. MOERS and J.J. STEGGERDA

Department of Inorganic Chemistry, Catholic University, Toernooiveld, Nijmegen (The Netherlands)

(Received October 25th, 1973)

Summary

Solutions of $RhCl(PCy_3)_2$ react with O_2, N_2, C_2H_4, CO and H_2 to give *trans*-$RhClA(PCy_3)_2$ (A = O_2, N_2, C_2H_4 and CO, Cy = cyclohexyl) and $RhClH_2(PCy_3)_2$; the spontaneous formation of the rather air-stable $RhCl(PCy_3)_2N_2$ is ascribed to a combination of the steric requirements and electronic properties of the phosphine ligand.

Tricyclohexylphosphine (PCy_3), like other bulky phosphines, is effective in stabilizing unusual coordination numbers and valence states [1, 2]. In the reaction of PCy_3 with $RhCl_3 \cdot 3H_2O$ no reduction to the Rh^I valence state occurs, but instead inter alia $Rh^{II}Cl_2(PCy_3)_2$ is formed [2]. Although the existence of $Rh^{III}Cl_3(PCy_3)_3$ has been reported [3], we did not succeed in its preparation and we have not found an indication for a PCy_3/Rh ratio exceeding 2 in any other complex. In this paper we report the preparation of Rh^I tricyclohexylphosphine compounds by cyclooctene displacement from $[RhCl(C_8H_{14})_2]_2$ [4].

Addition of two moles of PCy_3 per mole of $[RhCl(C_8H_{14})_2]_2$ resulted in the rapid formation of ochrous $[RhCl(PCy_3)(C_8H_{14})]_2$ (I). The solvated C_8H_{14}-free complex $RhCl(PCy_3)_2(S)$ (S = solvent molecule) was rather slowly formed (20 min stirring) by reaction of either 4 moles or an excess (8 moles) of PCy_3 (Rh/PCy_3 = 1/2, resp. 1/4) with $[RhCl(C_8H_{14})_2]_2$ in C_6H_6, and was isolated as a lilac precipitate of yet not fully identified nature. When $[RhCl(C_2H_4)_2]_2$ was used, yellow *trans*-$RhCl(C_2H_4)(PCy_3)_2$ (II) was obtained. The lilac product is unstable in the solid state, it decomposes within a few hours under vacuum and somewhat more slowly under nitrogen. It immediately turns brown upon exposure to air. In solution, however, $RhCl(PCy_3)_2(S)$ reacts rapidly with oxygen to give the grayish-blue adduct *trans*-$RhCl(O_2)(PCy_3)_2$ (III), while the dinitrogen adduct *trans*-$RhCl(N_2)(PCy_3)_2$ (IV) is formed when a solution of

$RhCl(PCy_3)_2(S)$ is exposed to 1 atm of N_2 for five days. CO equally adds to $RhCl(PCy_3)_2(S)$ to yield the known *trans*-$RhCl(CO)(PCy_3)_2$ (V) [2].

$RhCl(PCy_3)_2(S)$, made in situ, catalyses the hydrogenation of cyclohexene in benzene at a rate which is about 40 times less than the rate of hydrogenation by $RhCl(PPh_3)_3$ under similar conditions [5]. The yellow dihydride $RhClH_2(PCy_3)_2$ (VI) and the corresponding $RhClD_2(PCy_3)_2$ (VII) can most conveniently be prepared by the reaction of $RhCl(PCy_3)_2(C_2H_4)$ with H_2 or D_2.

Satisfactory analyses of the compounds have been obtained. Infrared spectroscopic data are given in Table 1. The large variation in Rh—Cl stretching vibration frequencies suggests that in the complexes $RhClA(PCy_3)_2$, Cl and A are in *trans* positions as are the two bulky PCy_3 ligands. The dihydride (VI) has a different structure and its Rh—Cl stretching vibration frequency may not be compared with those of the other adducts.

TABLE 1

INFRARED SPECTROSCOPIC DATA FOR COMPOUNDS $RhCl(PCy_3)_2A$

A	IR absorptions (cm^{-1})	
	ν(Rh—Cl)	others
C_2H_4	294m	3077w, 3040w, 3017w (ν(CH)); 1510w (br), 1208m, 1183w; 950m, 933w (δ(CH))
CO	304m	1942vs (ν(CO)), 584s (δ(CO))
N_2	317m	2103vs (ν(NN)), 470m (ν(RhN))
O_2	328m	993m[a]
H_2	291m	2165(sh), 2120m (ν(Rh—H)), 622m(br) (δ(Rh—H))
D_2	291m	1560(sh), 1528m (ν(Rh—D))

[a]Not assigned. PCy_3 absorbs in the 800-900 cm^{-1} region where MO_2 modes normally are found [7].

We assume the bulkiness of tricyclohexylphosphine to be one of the causes of the formation of the dinitrogen adduct (IV). For PCy_3, neither formation of a tris-complex comparable to $RhCl(PPh_3)_3$ [5] nor of a dimer comparable to $[RhCl(PPh_3)_2]_2$ [5] seems possible. Also adducts with C_6H_6 or C_8H_{14}, the other molecules present, seem to be labilized by steric influences of the two PCy_3 ligands. We therefore postulate the transient existence of the 14 metal valence electron species $RhCl(PCy_3)_2$ as the N_2-bonding species to account for this spontaneous dinitrogen coordination, which has not been reported before for rhodium(I) complexes. The comparable rhodium—dinitrogen compound $RhCl(PPh_3)_2(N_2)$ has been prepared by an indirect method [6]. The high basicity of PCy_3 may facilitate the addition of N_2, and certainly improves the stability of $RhCl(PCy_3)_2(N_2)$, which is only partly decomposed by air upon standing overnight in C_6H_6 or $CHCl_3$. At room temperature the N_2-ligand can be replaced by CO, but not by C_2H_4 or H_2. In similar reactions CO displaces C_2H_4, H_2, and O_2 from their adducts, to yield spectroscopically pure (V). Oxygen slowly replaces C_2H_4 and H_2 to give impure (III). In contrast to the behaviour of $RhCl(PPh_3)_2A$ (A = C_2H_4 or H_2) [5], $RhCl(PCy_3)_2A$ appears not to lose its coordinated molecule of C_2H_4 or H_2 on sweeping its solution with nitrogen.

A mixture of $[IrCl(C_8H_{14})_2]_2$ [4] and PCy_3 in C_6H_6 does not coordinate dinitrogen. Reactions with this system and further reactions with the rhodium system are currently under investigation.

We thank Mr. J. Diersmann for the elemental analyses and Mrs. A.W.P.G. Peters-Rit for the kinetic measurements.

References

1 F.G. Moers and J.P. Langhout, Rec. Trav. Chim. Pays-Bas, 91 (1972) 591.
2 F.G. Moers, J.A.M. de Jong and P.M.H. Beaumont, J. Inorg. Nucl. Chem., 35 (1973) 1915.
3 G.M. Intille, Inorg. Chem., 11 (1972) 695.
4 A. van der Ent and A.L. Onderdelinden, Inorg. Synth., 14 (1973) 92.
5 J.A. Osborn, F.H. Jardine, J.F. Young and G. Wilkinson, J. Chem. Soc. A, (1966) 1711.
6 L.Yu. Ukhin, Yu.A. Shvetsov and M.L. Khidekel', Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., (1967) 934.
7 V.J. Choy and C.J. O'Connor, Coord. Chem. Rev., 9 (1972) 145.